

SEMICONDUCTIVITY OF Cr-OXIDE FILMS DEPOSITED ON STAINLESS STEEL

A. M. Simões^{a*}, M. J. Carmezim^b, M. O. Figueiredo^c and M.
Da Cunha Belo^a

^a Instituto Superior Técnico, Chemical Eng. Dept., Av.
Rovisco Pais, 1049-001 Lisboa Codex, Portugal

^b Instituto Politécnico de Setúbal, ESTSetúbal, Mech. Eng.
Dept., Campus IPS, 2914 Setúbal, Portugal

^c CENIMAT and Materials Science Dept., FCT, Univ. Nova
de Lisboa, 2825 Monte de Caparica, Portugal

ABSTRACT

The electronic properties are important regarding the protective character of passive films on metals that exhibit a semiconductor or insulator behavior [1-6]. Several studies can be found in the literature on the semiconductivity of passive iron [7-10], for which n-type semiconductivity has been proven. For passive chromium, results in the literature suggest that, although the properties may change deeply with the conditions of film formation and applied potential, the electronic behaviour tends to correspond to a p-type semiconductor [5,11,12]. Passivity of stainless steels is usually attributed to the formation of a chromium-enriched oxide thin film on the surface.

Most of the characterisation of oxide films has been either on anodic films or on films formed thermally [4,6]. This work deals with conversion films formed by chemical deposition from chromic acid solution plus heat treatment, on a stainless steel substrate [13]. By varying the temperature of the treatment, four types of structures were produced: amorphous, corundum- phase, spinel- phase and mixed oxide films. The films were studied in a borate-boric acid buffer solution (pH 8.4) by Mott-Schottky plots and photocurrent measurements. The amorphous films presented metallic behaviour. For the crystalline films both n- and p-type semiconductivity were observed, respectively above and below an apparent flatband potential. Doping densities evaluated from Mott-Schottky plots stand below 10^{20} cm^{-3} for the crystalline films, and decreased with the treatment temperature.

In contrast with the anodic films reported in literature, these conversion films presented direct and indirect electronic transitions. The photocurrent study revealed three different transitions. A sub-gap transition at 2.0 eV was associated with the iron transition [14]. Above the gap, an indirect transition at 2.9 eV and a direct transition at 3.5 eV were found for films treated at 973 K and at 1073 K, and can be associated with Cr_2O_3 [5]. The film treated at 1223 K (spinel oxide) revealed distinct behavior in terms of photoelectrochemical response, with a transition at 4.2 eV.

A bi-polar model for the semiconductivity of the films was derived from these results. In this model, the films were described as thick layers of chromium oxide, containing iron and manganese. The existence of cation vacancies near the surface can be responsible for the n-type semiconductivity,

whereas excess of cations in the inner part justifies the observed p-type semiconductivity.

References:

1. H.Gerischer, Corros. Sci., 29 (1989) 257.
2. H.Gerischer, Corros. Sci., 31 (1989) 81.
3. A. DiPaola, Electrochimica Acta, 34 (1989) 203.
4. A. M. P. Simões, M.G.S. Ferreira, B. Rondot and M. da Cunha Belo, J. Electrochem. Soc., 137 (1990) 82.
5. C. Sunseri, S. Piazza and F. Di Quarto, J. Electrochem. Soc., 137 (1990) 2411.
6. N.E. Hakiki, M. da Cunha Belo, A. M. P. Simões, M.G.S. Ferreira, J. Electrochem. Soc., 145 (1998) 3821.
7. P.C. Searson, R.M. Latanision, U. Stimming, J. Electrochem. Soc., 135 (1988) 1358.
8. L.M. Abrantes, L.M. Peter, J. Electroanal. Chem., 150 (1983) 593.
9. S.M. Wilhelm, K.S. Yun, L.W. Ballenger, N. Hackerman, J. Electrochem. Soc., 126 (1979) 419.
10. M. Büchler, P. Schmuki, H. Böhni, J. Electrochem. Soc., 145 (1998) 609.
11. M. Metikos-Hukovic and M. Ceraj-Ceric, J. Electrochem. Soc., 134 (1987) 2193.
12. E.W.A. Young, J.H. Gerretsen and J.H.W. de Wit, J. Electrochem. Soc., 134 (1987)
13. M.J. Carmezim, F.G. Carvalho, M.O. Figueiredo, Thin Sol. Films, 258 (1995) 194.
14. J.B. Goodenough, Les Oxydes des Métaux de Transition, Gauthierrs-Villars, Paris, 1967.

* corresponding author e-mail:
pcsimoes@alfa.ist.utl.pt, tel:+351 21 8417234,
Fax: +351 21 8404589